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The $\nu_{14}(b_{2u})$ Mode of Benzene in S_0 and S_1 and the Distortive Nature of the π Electron System: Theory and Experiment

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This paper addresses a current debate concerning the origins of the D_{6h} symmetry of benzene[1−3] by discussing the changes which the b_{2u} vibrational modes undergo upon electronic excitation. Spectroscopic evidence, backed by ab-initio calculations, supports the view expressed in ref 2 that this symmetry is due to σ bonding, which overcomes the tendency of the π electrons to distort the molecule to a D_{3h} structure.

The symmetry analysis of the vibrational modes of benzene by Wilson[4] was one of the first demonstrations of the power of group theoretical methods in molecular spectroscopy. Subsequent work focused heavily on the development of suitable force fields that will provide a unified method for the calculation and assigned of vibrational spectra of benzene and its derivatives. Early on it was noticed that b_{2u} modes are unique, in that the calculated frequency of one of the modes (~1600 cm^{-1}) was too high as compared to experiment.[5] An ad-hoc correction of the Urey−Bradley force field, which included a term for stabilization of a Kekulé form (rather than a delocalized structure), had to be added for a successful fitting of the data.[5] In an attempt to account for the observed low values of the b_{2u} frequencies of benzene, Berry proposed that the π electrons tend to distort the $S_0(^1A_{1g})$ ground state to a D_{3h} structure.[6]

The $\nu_{14}(b_{2u})$ vibrational mode of the $S_1(^1B_{2u})$ state was never observed in the conventional (one photon) $S_0 \rightarrow S_1$ absorption spectrum of benzene and was first reported in a two photon study.[7] It was found to be the most dominant vibronic feature, a fact that was ascribed to vibronic coupling.[8,9] The authors of ref 8 were the first to correctly assign the strongest peak to the $\nu_{14}(b_{2u})$ mode. Its frequency was considerably higher than that in the ground state (1570 vs 1309 cm^{-1}), a fact that was not accounted for. Furthermore, perdeuteration had a very small effect on the measured frequency (1564 and 1282 cm^{-1} in S_1 and S_0, respectively), showing that the atomic motions associated with this mode are largely due to the carbon atoms. Evidence for the skeletal predominance of this mode was extensively discussed by Goodman and co-workers.[10]

In a study on styrene and some of its derivatives,[11] we noticed that the corresponding mode (ν_{17} in styrene) behaved in the same way. An ab-initio calculation showed that this mode involves primarily ring motion, and unlike most of the in-plane modes that underwent a small frequency *decrease* on electronic excitation, this mode showed a pronounced frequency *increase*. This and the ongoing debate[1−3] prompted us to reconsider the benzene problem and check the behavior of the different vibrational modes upon excitation of the molecule from the $^1A_{1g}$ state to the $^1B_{2u}$ state. The calculation was done at the CIS/6-31+G level,[12] with a complete structure optimization of both states.[13] Frequencies were calculated at the harmonic approximation, as described in our previous papers,[11,14] and a uniform scaling of 0.89 and 0.85 was applied to in-plane and out-of-plane modes, respectively, in both S_0 and S_1. The results are in good agreement with previous ab-initio calculations on this molecule [refs 15 (for S_0) and 16−18 (for S_1)] and with experimental data.[19−21] In this Communication we focus attention on the observed up-shift in the ν_{14} mode's frequency and propose a rationale for the large increase in the calculated force constant of this mode.

Figure 1 shows a correlation diagram, connecting the ground state vibrational modes with the excited state ones. The abnormal rise in the $\nu_{14}(b_{2u})$ mode's frequency is clearly seen. Figure 2 shows the calculated vector displacement diagram of the two b_{2u} modes of benzene in both electronic states (see refs 17 and 19 for similar results). In the ground state, the two modes are nearly equivalent, with both carbon and hydrogen atoms contributing to the motions. The only difference is that in the lower frequency mode the hydrogen atoms move in phase with the carbon atoms, while in the higher frequency mode their motion is 180° out of phase. In the excited state, the two modes may be viewed as arising from positive and negative combinations of the ground state modes: the motions of the hydrogen atoms are calculated to be completely separated from those of the carbon atoms. Mode 14 is seen to involve only displacements of carbon atoms, while in mode 15, only hydrogen atoms move, and the carbon atoms are stationary. This result is also reflected by the reduced masses of these modes, 11.80 (ν_{14}) and 1.01 (ν_{15}) amu. An order of magnitude increase in the force constant of the ν_{14} mode is calculated upon excitation: 22.7 mdyn/Å in S_1, compared to 1.5 and 2.5 mdyn/Å for the ground state modes ν_{14} and ν_{15}, respectively. A calculation done on C_6D_6 also showed that the ν_{14} mode involves essentially only carbon atoms in motion, as reflected by the fact that the reduced mass is 11.98 amu. The force constant is 23.0 mdyn/Å (as in the protonated isotopomer), leading to the same vibrational frequency, 1608 cm^{-1}. The calculated reduced mass of the ν_{15} mode is 2.01 amu, and only the deuterons are in motion.

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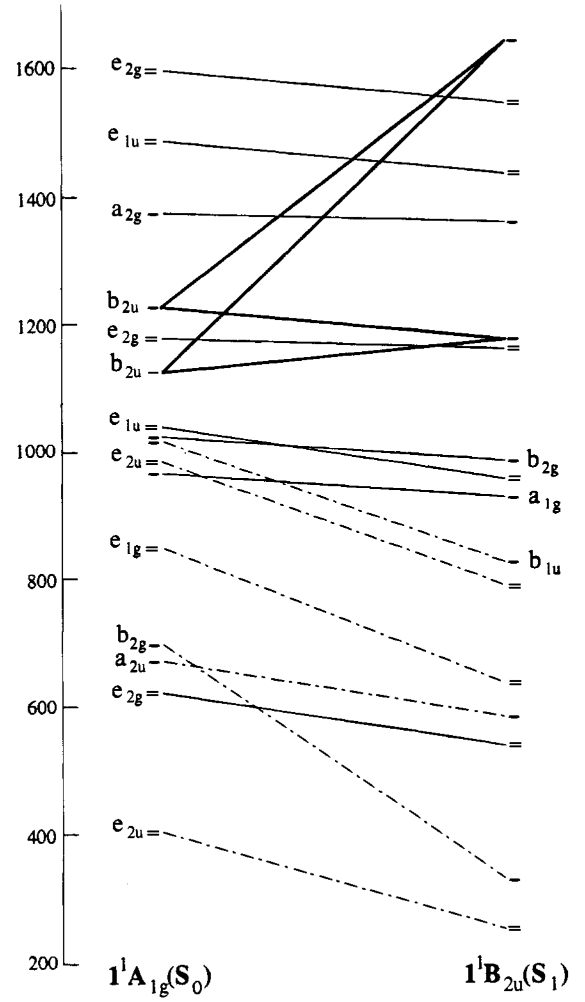

Figure 1. Diagram showing the correlation between S_0 and S_1 vibrational modes of benzene, as calculated at the CIS/6-31+G level (CH stretch modes are not shown).

It is well known[22] that the $S_0 \rightarrow S_1$ transition involves excitation of an electron from the degenerate pair of HOMOs (e_{1g}) to the pair of LUMOs (e_{2u}). In the process, the ring is calculated to expand from a CC bond length of 1.390 to 1.418 Å (experimental values are 1.397 and 1.435 Å, respectively[23]). The transfer of a π electron from a bonding to an antibonding orbital is expected, in general, to weaken the bonds and lead to smaller force constants and lower vibrational frequencies. This is indeed the case for most of the vibrational modes of benzene (Figure 1); the counterintuitive behavior of the ν_{14} mode indicates a different physical situation.

The D_{6h} symmetry of the benzene molecule has been traditionally ascribed to the π electronic delocalization.[24] This view has been challenged by some recent theoretical studies,[2] which argue that it is the σ frame that ensures the symmetric D_{6h} structure, while the π electrons tend to prefer a Kekulé type D_{3h} distortion. The *only* coordinate along which this distortion can take place is of b_{2u} symmetry. The work of Shaik, Hiberty, and co-workers was criticized on theoretical grounds by Glendening et al.,[3] who argued that delocalization effects act to strongly stabilize the symmetric structure of benzene, in accord with the classical concepts. Both theories have so far relied on theoretical and computational arguments, with little direct experimental support. We propose that the observed increase of the $\nu_{14}(b_{2u})$ mode's frequency may be used to probe the validity of the arguments.

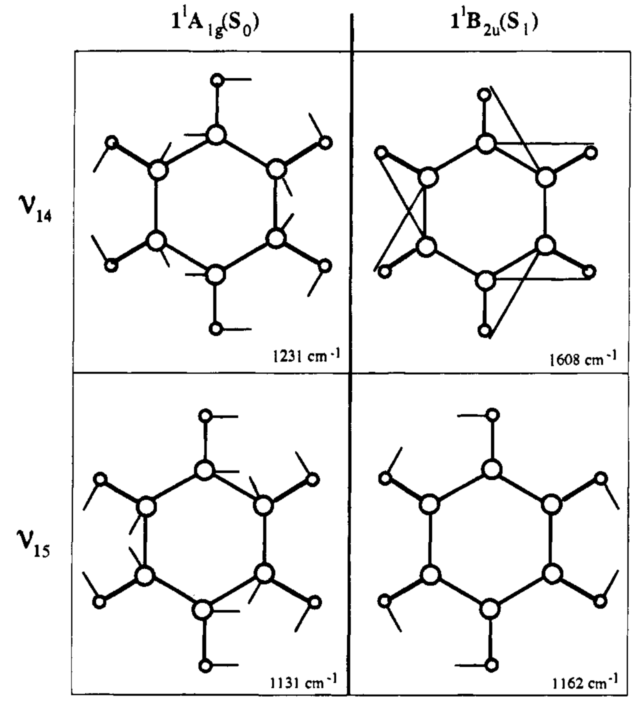

Figure 2. Calculated frequencies and vector displacements of the atoms in the b_{2u} modes ν_{14} and ν_{15} in the ground and first electronically excited states of benzene.

According to the theory of Shaik and Hiberty,[2] promotion of a π electron to an antibonding orbital reduces the π distortivity power and thus helps to reveal more clearly the influence of the σ potential on the b_{2u} mode. Therefore, the restoring force for motion of the carbon atoms along this coordinate should be strengthened, and the corresponding vibrational frequency should in fact increase, as observed experimentally. The traditional view would predict the opposite effect.

It is concluded that the apparently anomalous increase in the frequency of the $\nu_{14}(b_{2u})$ mode of benzene is accounted for in a natural way if the notion that π electrons tend to distort the molecule away from the D_{6h} symmetry is adopted. Furthermore, the avoided crossing theory of Shaik and Hiberty[2] predicts that the increase in the force constant will be mode selective: only the ν_{14} mode will be thus affected. It is the mode along which the ground ($^1A_{1g}$) and the $^1B_{2u}$ states are generated by the avoided crossing of the two Kekulé structures. It is noted that a similar frequency rise is observed also in the $\nu_{21}(b_{2u})$ mode of naphthalene upon excitation to the $^1B_{2u}$ state,[25,26] which may be explained in the same way. The avoided crossing model appears to account for this observation, the separation of the C and H b_{2u} modes, and other features, as will be discussed in a forthcoming paper.[27]

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